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Improving the sensitivity of *J* coupling measurements in solids with application to disordered materials

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It has been shown previously that for magic angle spinning (MAS) solid state NMR the refocused INADEQUATE spin-echo (REINE) experiment can usefully quantify scalar (*J*) couplings in disordered solids. This paper focuses on the two *z* filter components in the original REINE pulse sequence, and investigates by means of a product operator analysis and fits to density matrix simulations the effects that their removal has on the sensitivity of the experiment and on the accuracy of the extracted *J* couplings. The first *z* filter proves unnecessary in all the cases investigated here and removing it increases the sensitivity of the experiment by a factor ~1.1–2.0. Furthermore, for systems with broad isotropic chemical shift distributions (namely whose full widths at half maximum are greater than 30 times the mean *J* coupling strength), the second *z* filter can also be removed, thus allowing whole-echo acquisition and providing an additional $\sqrt{2}$ gain in sensitivity. Considering both random and systematic errors in the values obtained, *J* couplings determined by fitting the intensity modulations of REINE experiments carry an uncertainty of 0.2–1.0 Hz (~1–10 %). [http://dx.doi.org/10.1063/1.4948965]

I. INTRODUCTION

Scalar (*J*) couplings in NMR are a rich, but relatively under-exploited source of structural information for disordered solids. As an indirect coupling mediated by bonding electrons, the *J* coupling is extremely sensitive to the local environment around each atom, revealing the connectivity of the network,[1–4] along with information concerning the length and angle between particular bonds.[5–8] The impressive achievements of NMR crystallography[9–14] and the *ab initio* methods developed in parallel for the calculation of *J* couplings[15,16] suggest that a similar experimental-computational approach, enhanced by medium-range information from the *J* couplings, could provide an improved understanding of the structure of non-crystalline solids. However, whereas chemical shifts can be read directly from one-dimensional NMR spectra, in solids, line broadening caused by anisotropic interactions and distributions of isotropic chemical shifts masks the splitting of the peaks induced by the *J* coupling, whose intensity must therefore be derived from the spin-echo modulations of one- or two-dimensional spectra[6,17–20] A library of experimentally determined *J* coupling values has thereby been assembled for a wide range of chemical bonds.[21–28] In particular, the refocused INADEQUATE spin-echo (REINE) experiment has been used to measure *distributions* of *J* coupling strengths in cellulose[29] and in a phosphate glass.[30] These distributions offer far finer structural insights than do the average couplings revealed by simple spin-echo (*J* resolved) experiments.[30]

More than the protracted nature of the measurements however, it is the lower sensitivity of the multidimensional pulse sequences that is the main barrier to their applicability to a wider range

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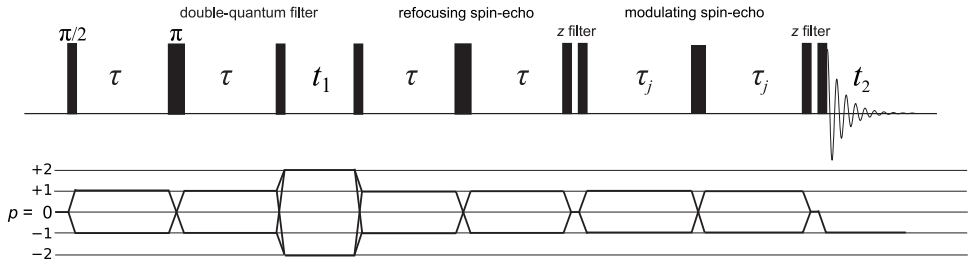

FIG. 1. Pulse sequence and coherence transfer pathway diagram for the refocused INADEQUATE spin-echo (REINE) sequence. Three versions of the experiment are considered here (*viz.* with both z filters, only the second, or no z filters), and are denoted A, B and C, respectively.

of systems, recent improvements in NMR hardware notwithstanding. In the REINE experiment (Figure 1), the double-quantum filter separates the signal from differently bonded pairs according to the sum of their individual chemical shifts. The refocusing spin-echo increases the efficiency of the sequence for disordered solids,[1] while the final spin-echo element in the sequence encodes the chemical shift-separated signals with the J coupling strength of the corresponding pairs. The z filters either side of the modulating spin-echo ensure that only the in-phase NMR signal is acquired during the detection period. An obvious way to improve the sensitivity of the REINE experiments is simply to remove the z filters. The present report demonstrates that these elements of the pulse sequence are not essential to the accuracy of the associated measurements. In this context, the different sources of error and the intrinsic precision of the spin-echo approach to measuring scalar couplings are also discussed. The different intensity modulations predicted from a product operator analysis of the different versions of the REINE experiment are verified for simulated crystalline, disordered and glassy systems.

II. THEORY

A. Product operator analysis

The J-modulating spin echo in the REINE pulse sequence (Figure 1) is flanked by two z filters,[31] whose role is to suppress unwanted anti-phase contributions to the spectra. To ascertain the nature of these distortions, a product operator[32] analysis is presented, starting from the previously published results for the refocused INADEQUATE experiment.[33]

The calculations consider isolated spin-1/2 pairs (A and B) interacting via a J coupling under solution-like conditions. That is, (i) the spinning frequency is high enough to completely eliminate homonuclear dipolar interactions (over an integer number of rotor cycles), (ii) rotational resonance conditions are avoided, allowing anisotropic chemical shift interactions to be neglected,[34] and (iii) the decoupling is efficient enough (or the proton content low enough) for heteronuclear dipolar couplings to be neglected. (This is typically the case for ^{31}P or ^{29}Si nuclei in oxide glasses, for instance.) The density matrix at the end of the refocused INADEQUATE sequence is[33]

$$\sigma_{\mathrm{rI}} = \frac{M_0^{\mathrm{A}} + M_0^{\mathrm{B}}}{2}\left(S_\tau^2\left(\mathrm{A}_y + \mathrm{B}_y\right) + S_\tau C_\tau\left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right)\right) \tag{1}$$

where M_0^{A} and M_0^{B} are the magnitudes of the transverse magnetization on spins A and B, respectively, created by the initial pulse. The following abbreviations have been introduced for the build-up of the in-phase (A_y, B_y) and anti-phase ($2\mathrm{A}_x\mathrm{B}_z$, $2\mathrm{A}_z\mathrm{B}_x$) single-quantum coherences over the four τ delays in the sequence (see Figure 1):

$$S_\tau^2 = \sin^2(2\pi J\tau) \tag{2}$$

$$S_\tau C_\tau = \sin(2\pi J\tau) \times \cos(2\pi J\tau) \tag{3}$$

The same abbreviation scheme is used below for the sine and cosine evolution of the operators during the τ_j and t_2 delays.

Assuming that the parameters of the first z filter are set so as not affect the in-phase signal, i.e. the delay is not unnecessarily long and the phase cycle removes the anti-phase terms,[33] Equation (1) becomes,

$$S_\tau C_\tau \left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right) \xrightarrow{zf1} Z_1 S_\tau C_\tau \left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right) \tag{4}$$

with $Z_1 = 0$ for a perfect z filter, $Z_1 = 1$ in the absence thereof. Both in-phase and anti-phase coherences evolve under the scalar coupling during the J-modulating spin echo,

$$S_\tau^2\left(\mathrm{A}_y + \mathrm{B}_y\right) \xrightarrow{2\pi J\tau_j} S_\tau^2 C_{\tau_j}\left(\mathrm{A}_y + \mathrm{B}_y\right) - S_\tau^2 S_{\tau_j}\left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right) \tag{5}$$

$$\begin{aligned} Z_1 S_\tau C_\tau \left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right) \xrightarrow{2\pi J\tau_j} & Z_1 S_\tau C_\tau C_{\tau_j}\left(2\mathrm{A}_x\mathrm{B}_z + 2\mathrm{A}_z\mathrm{B}_x\right) \\ & + Z_1 S_\tau C_\tau S_{\tau_j}\left(\mathrm{A}_y + \mathrm{B}_y\right) \end{aligned} \tag{6}$$

Gathering the terms in Equations (5) and (6), and accounting for the effect (Z_2) of the second z filter on the anti-phase coherences, the detectable[39] density matrix evolves during the detection period as:

$$\begin{aligned} \sigma(\tau, \tau_j t_2) = & \frac{M_0^{\mathrm{A}} + M_0^{\mathrm{B}}}{2}\left(\mathrm{A}_y + \mathrm{B}_y\right) \\ & \times \left(\left(S_\tau^2 C_{\tau_j} + Z_1 S_\tau C_\tau S_{\tau_j}\right) C_{t_2} + \left(Z_1 Z_2 S_\tau C_\tau C_{\tau_j} - Z_2 S_\tau^2 S_{\tau_j}\right) S_{t_2}\right) \end{aligned} \tag{7}$$

Table I compares the τ build-up, z-filter attenuation, and τ_j evolution of the different terms in Eq. (7). Considering first the build-up of each of the four terms, under solution-like conditions, optimal INADEQUATE efficiency will be achieved for $J\tau = 1/4$ and terms 2 and 3 disappear. In this case, the cosine J-modulation of the REINE signal (term 1) will be observed as long as the second z filter removes anti-phase contributions to the spectra (term 4). In solids however, as described previously by Lesage *et al.*,[1] transverse (T_2') dephasing means that the optimal value of $J\tau$ ($J\tau_{\mathrm{opt}}$) is no longer the root of the cosine build-up terms (see Figure S1 in the supplementary material).[35] These therefore become important and contribute sine J-modulated in-phase REINE intensity (term 2 in Table I). In other words, the first z filter eliminates a sizeable proportion of the total in-phase signal. With applications to disordered materials (broad lineshapes) in mind, the hypothesis investigated here regarding the second z filter (terms 3 and 4) is that integrated intensity from the anti-phase doublets tends to zero when the chemical shift distribution is much broader than the J splitting.

B. Sensitivity

Ignoring anti-phase terms, which make a zero net contribution to the spectrum on average, the total intensity accumulated in a REINE experiment at a frequency Ω in the ω_2 domain is

$$S\left(\Omega, \tau, \tau_j; \omega_2\right) = \mathcal{G}\left(\Omega; \omega_2\right) \sum_{\tau_j=0}^{\tau_j^{\max}} \sigma\left(\tau, \tau_j\right) \times \exp\left[-\frac{2\tau_j}{T_2'}\right] \tag{8}$$

TABLE I. List of terms contributing to refocused INADEQUATE spin-echo spectra.

	Term	Signal type	Build-up function	J evolution	z-filter attenuation
1	$S_\tau^2 C_{\tau_j} C_{t_2}$	in-phase	$\sin^2(2\pi J\tau)$	$\cos(2\pi J\tau_j)$	none
2	$Z_1 S_\tau C_\tau S_{\tau_j} C_{t_2}$	in-phase	$\sin(2\pi J\tau)\times\cos(2\pi J\tau)$	$\sin(2\pi J\tau_j)$	Z_1
3	$Z_1 Z_2 S_\tau C_\tau C_{\tau_j} S_{t_2}$	anti-phase	$\sin(2\pi J\tau)\times\cos(2\pi J\tau)$	$\cos(2\pi J\tau_j)$	$Z_1\times Z_2$
4	$Z_2 S_\tau^2 S_{\tau_j} S_{t_2}$	anti-phase	$\sin^2(2\pi J\tau)$	$\sin(2\pi J\tau_j)$	Z_2

where $\mathcal{G}(\Omega;\omega_2)$ is the functional form of the NMR spectrum, which for a powder sample under magic angle spinning (MAS) is typically a Gaussian distribution of overlapping Lorentzians. Note that the optimal value of τ will in practice be defined by JT_2', as described in the supplementary material.[35] Comparing now versions of the REINE experiment run under identical conditions, but either with or without the second z filter, the sensitivity ratio between the two can be written

$$\frac{S_{z1+z2}(\Omega,\tau,\tau_j;\omega_2)}{S_{z1}(\Omega,\tau,\tau_j;\omega_2)} = \left|\sum_{\tau_j=0}^{\tau_j^{\max}} \frac{S_\tau^2 C_{\tau_j} + S_\tau C_\tau S_{\tau_j}}{S_\tau^2 C_{\tau_j}}\right| \tag{9}$$

where the absolute value taken in Equation (9) ensures that positive and negative intensities are accounted for equivalently.

Evaluating Equation (9) for different (reasonable) values of JT_2' (Table II and Figure S1a)[35] shows that omitting the second z filter is particularly effective when the J modulation occurs *slowly* with respect to the decay of the spin-echo. For the values of JT_2' considered here, the simplified version of the REINE experiment is, according to this analysis, up to twice as sensitive.

III. METHODS

A. Strategy

Figure 2 illustrates the strategy adopted here to investigate the viability of the proposed pulse sequence simplifications. One-dimensional (1D) REINE spectra are simulated for 10 values of τ_j (Figure 2(a)). The evolution under the J coupling of each point in the spectrum is then fit using an appropriate function (Figure 2(b), 2(c)), based on the theoretical analysis presented in Section II. (This approach reproduces the experimental workflow for measuring J coupling distributions using the REINE sequence,[29,30] the simulated spectra corresponding to slices of 2D spectra) The values obtained from the fits are then compared with those initially simulated (Figure 2(d)).

The spectra consist of two Gaussian distributions of n overlapping J doublets, whose splitting is correlated with the chemical shift of the simulated atom pairs. A third atom is included in the simulations, coupled through space, but not bonded to the other two. Starting from parameters representing the interactions between phosphate groups in a glass, several series of simulations are performed for different Gaussian linewidths (with n increasing/decreasing in proportion) to evaluate the applicability of the proposed simplifications for a variety of physical systems. The three versions of the experiment considered here (*viz.* with both z filters, only the second, or no z filters) are denoted A, B and C, respectively, from now on. Note that rotational resonance and multi-spin effects are not considered here.

B. Simulation parameters

The different versions of the REINE NMR experiment were simulated using SIMPSON 4.1.1,[36] for sets of three dipolar coupled ^{31}P nuclei with different isotropic chemical shifts. For 10 values of

TABLE II. Sensitivity of the refocused INADEQUATE spin-echo experiment without versus with the second z filter.

JT_2'	$J\tau_{\text{opt}}$[a]	τ_j^{zcb}	$S_\tau C_\tau$[c]	S_τ^2	Sensitivity[d] ($\tau_j^{\max}=\tau_j^{\text{zc}}$)	Sensitivity[d] ($\tau_j^{\max}=1.5\times\tau_j^{\text{zc}}$)
0.2	0.089	$4.6\times\tau_{\text{opt}}$	0.450	0.281	1.57 (0.18)	2.02 (0.16)
0.5	0.161	$2.1\times\tau_{\text{opt}}$	0.448	0.721	1.46 (0.71)	1.32 (0.52)
1.0	0.201	$1.5\times\tau_{\text{opt}}$	0.289	0.908	1.27 (1.00)	1.11 (0.79)

[a]The optimal (in terms of sensitivity) build-up time (τ) for the refocused INADEQUATE block (see Figure 1).
[b]The value of τ_j at the zero-crossing (ZC)—at which term 1 + term 2 = 0 (see Table I).
[c]See Equation (3).
[d]Equation (9) evaluated for the values of $\tau_j^{\max}$ listed in this table. The normalized absolute sensitivity of the refocused INADEQUATE spin-echo experiment with the second z filter is shown in parentheses (see also Figure S1a).[35]

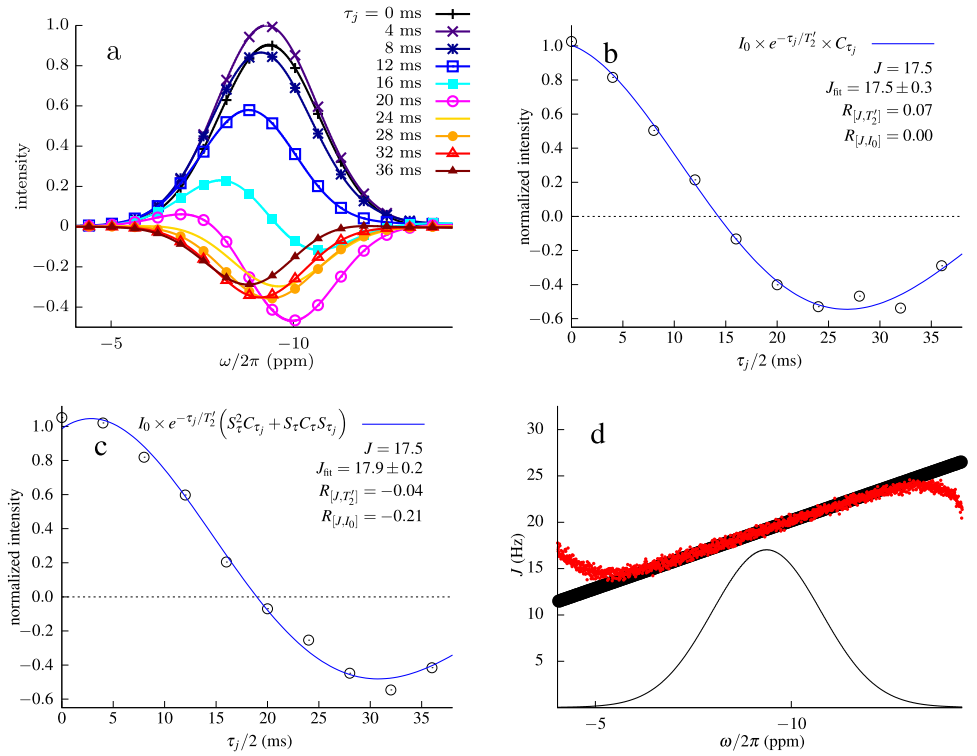

FIG. 2. (a) Simulated refocused INADEQUATE spin-echo (REINE) spectra with no z filters and the values of τ_j (see Figure 1) listed in the inset. (b, c) Fits (solid lines) of the evolution as a function of τ_j of the intensity at −8.2 ppm in REINE spectra simulated (b) with two z filters and (c) without z filters. From top to bottom, the values listed on the right of panels (b) and (c) are the simulated and fitted J coupling, and the correlation coefficients between the fitting parameters. Gaussian noise with a standard deviation of 0.05 was added to the separate intensity modulations (vs. τ_j, normalized to a maximum of 1.0) obtained for each point in the frequency domain. (d) Simulated (thick black line) and fitted (red dots) J coupling strengths, above the corresponding REINE spectrum (two z filters) at $\tau_j = 0$.

τ_j (0–36 ms, in 4 ms increments), simulations of experiments A, B and C were repeated n times, then co-added with Gaussian weighting, with the isotropic chemical shift and scalar coupling of the ^{31}P nuclei increased linearly, the latter from 11.5 to 26.5 Hz, and n being proportional to the width of the chemical shift distribution. The dipolar and (mean) scalar couplings between the spins were set to the values determined by Fayon *et al.* for crystalline TiP_2O7.[34] The range of the J coupling distribution was defined based on the ones measured experimentally for a cadmium phosphate glass.[30] The chemical shift tensors and distributions of isotropic shifts were defined so as to obtain representative models of crystalline and glassy lead metaphosphates,[37] and a magnesium metaphosphate glass.[38] The spin system and chemical shift distribution parameters used are listed in Table SI in the supplementary material,[35] along with a representative SIMPSON input file. Experiments B and C were simulated under 12.5 kHz magic angle spinning. For experiment A however, since the simulations yield identical results whether the anisotropic interactions are considered or not (Table SII),[35] time consuming magic angle spinning calculations were not required.

C. Analysis

The evolution under the scalar coupling of each point in the resulting spectra was fit using either

$$I(\tau_j) = I_0 \times C_{\tau_j} \times \exp\left[-\frac{2\tau_j}{T_2'}\right] \tag{10}$$

for experiment A, or

$$I(\tau_j) = I_0 \times \left(S_\tau^2 C_{\tau_j} + S_\tau C_\tau S_{\tau_j}\right) \times \exp\left[-\frac{2\tau_j}{T_2'}\right] \tag{11}$$

for experiments B and C, after normalizing the data and adding Gaussian noise ($\sigma = 0.05$) and an exponential decay ($T_2' = 15$ or 45 ms). The results obtained using custom-written Python 2.7 scripts were confirmed by using the fit command in Gnuplot 4.6.6. for a subset of the data. Fitting errors and the correlations between the fitting parameters were obtained from the associated covariance matrix.

Equation (9) was evaluated for the values of $\tau_j^{\max}$ listed in Table II, by calculating the values of the numerator and denominator for 10,000 points equally spaced from $\tau_j = 0$ to $\tau_j^{\max}$. (Doubling the number of points considered does not modify the sensitivity ratio.)

IV. RESULTS AND DISCUSSION

A. Simplified experiments

Comparing parts (b) and (c) of Figure 2 highlights the additional presence of term 2 (Table I) in the J modulation of the REINE intensity in the absence of z filters. Figure 3 shows that this sine modulation can be accounted for accurately by modifying the fitting function according to the product operator analysis (i.e. by using Equation (11) instead of Equation (10)). Indeed for all the linewidths considered here, the scalar couplings fit to the intensity modulations of experiment B are at least as accurate as those obtained from experiment A, the mean errors in the fitted values being low (< 0.2 Hz) for all but the broadest chemical shift distribution. (As discussed at greater length below, the fitted values diverge more substantially for the broadest line because of peak overlap.) With experiment C in contrast, the discrepancies between the simulated and fitted scalar couplings are large (> 0.6 Hz on average) for the narrowest line, but decrease sharply as the disorder of the simulated system increases (mean error = 0.21 and 0.26 Hz for FWHM of 4.8 and 7.5 ppm, respectively).

This effect is emphasized in Figure S2, which compares the scalar coupling distributions obtained from simulations of experiments A and C, with no noise added, for different widths of the chemical shift distribution.[35] Figure S3 confirms that the deviations stem from the anti-phase terms

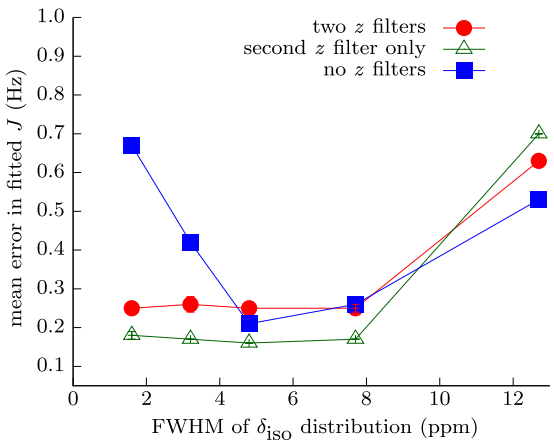

FIG. 3. Mean error, as a function of the full width at half maximum (FWHM) of the underlying chemical shift distribution, in the J coupling strengths fit to the intensity variations of refocused INADEQUATE spin-echo spectra. Gaussian noise with a standard deviation of 0.05 was added to the separate intensity modulations (normalized to a maximum of 1.0) obtained for each point in the frequency domain. The error bars, representing the standard deviation of five repeat fits, are smaller than the point markers. The physical systems corresponding to each FWHM are described in Table SI in the supplementary material.[35]

(3 and 4 in Table I), whose integrated intensity decreases markedly (by up to ~70 %) as the chemical shift distribution broadens.[35] Note that although the specific values quoted here for the errors are parameter-dependent, the trends with respect to the linewidths and between the different versions of the REINE experiment are reproduced for a wide range of values—namely, of the standard deviation of the Gaussian noise (Figure S4a,b), the MAS frequency and magnitude of the dipole-dipole couplings (Figure S5a–c), and the range of the J coupling distribution (Figure S5d).[35] In particular, although the zero crossing in the intensity modulation occurs later for experiments B and C, these in fact yield more (not less) accurate values than experiment A when T_2' is shorter (Figure S4c). Furthermore, the fitting variables remain uncorrelated throughout (Table SIII). In summary, provided the chemical shift distribution is very broad with respect to the mean J coupling (FWHM $> 30 \times \bar{J}$), the REINE experiment can be performed without z filters without compromising on the accuracy of the results. In line with the predicted gains in sensitivity (+11–102 %, see Table II), the removal of the first z filter makes experiments B and C 1.23 times more sensitive than experiment A, as measured from the total integrated intensity for the set of simulations whose results are summarized in Figure 3. Experiment C can moreover be run with whole-echo acquisition, leading to an extra $\sqrt{2}$ gain in sensitivity.

B. Sources of error

The mean errors in the fitted J coupling strengths range from ~0.2 to ~0.7 Hz (Figure 3) but the fitting errors range only from 0.2 to 0.3 Hz (see Figure 2(b), 2(c) for example). Indeed, for all versions of the REINE experiment indeed, the modulation of a given point in the spectrum is an average of the intensity variations of several overlapping doublets. This is illustrated in Figure S2a (for which no noise was added to the simulated data),[35] where the fitted values are slightly overestimated to the left of the peak maximum, and underestimated to the right, where the neighboring doublets toward the center of the distribution have respectively a greater and smaller splitting than that of the underlying doublet, were it to be considered in isolation. Averaging induces more substantial errors when two (or more) chemical shift distributions overlap, as the difference between the mean splitting and those of the individual doublets is likely much greater. Nevertheless, the simulations performed here for overlapping lines suggest that even for large (>15 Hz) differences between the overlapping doublets, ±1 Hz is a conservative estimate of the systematic error induced.

Finally, should one wish to trade accuracy for sensitivity and use experiment C for relatively well ordered systems, these results suggest that the distortions from the anti-phase contributions can be covered by simply adding 0.4 Hz to the errors output by the fitting algorithm.

V. CONCLUSION

The simplifications and the corresponding gains in sensitivity discussed in this paper should make the precise measurement of near-pair-specific scalar couplings more routine in a number of disordered systems. In practice furthermore, omitting the two z-filter elements should make the REINE sequence easier to implement, with a higher tolerance for slightly imperfect pulse powers or durations. Comparing experimental values with those calculated from first principles[15,16] should allow both a refinement of the algorithms and, eventually, a better understanding of the bonding and structural variations in non-crystalline solids, possibly in combination with the precise measures of coherence lifetimes that this approach provides.

ACKNOWLEDGEMENTS

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